

Liquid elasticity length and universal dynamic crossovers

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We discuss two main universal dynamic crossovers in a liquid that correspond to relaxation times of 1 ps and $10^{-7} - 10^{-6}$ s. We introduce the concept of liquid elasticity length d_{el} . At room temperature, d_{el} is several Å in water and increases to 0.01 mm in honey and 1 mm in tar. We show that on temperature decrease, d_{el} crosses the fundamental lengths of the system, medium-range order d_m and system size L . We discuss how $d_{el} = d_m$ and $d_{el} = L$ correspond to the two dynamic crossovers.

A conceptually simple phenomenon, freezing of liquid into glass, has turned out to be one of the most difficult problems in condensed matter physics, the problem of glass transition [1]. Analyzing the current state of the field, Dyre recently suggested that glass transition itself is not a big mystery: it universally takes in any liquid when its relaxation time τ exceeds the time of experiment at the glass transition temperature T_g [2]. He proposed that the challenges lie above T_g [2].

If we consider the changes in molecular dynamics in a liquid on lowering the temperature, we find two dynamic crossovers. The first crossover is at high temperature at $\tau \approx 1$ ps, at which dynamics changes from exponential Debye relaxation to SER, $q(t) \propto \exp(-(t/\tau)^\beta)$, where q is a relaxing quantity and $0 < \beta < 1$. This crossover is universal, i.e. is seen in many systems [3, 4, 5, 6, 7]. SER describes a very sluggish dynamics: in the wide data range, it decays as a logarithm of time. As the temperature is lowered, we find another universal crossover, which takes place at lower temperatures that correspond to $\tau = 10^{-7} - 10^{-6}$ s [8, 9]. This crossover also marks the qualitative change in system's dynamics, and was attributed to the transition from the "liquid-like" to the "solid-like" behaviour. Note that although relaxation time at the second crossover is much larger as compared to the first one, it is still about 9–10 orders magnitude smaller than relaxation time at the glass transition. By definition, T_g corresponds to τ on the order of 10^3 s.

One hopes to find useful insights into the problem of glass transition if the origin of dynamic crossovers could be rationalized. In this paper, we discuss this problem in terms of elastic stresses that a liquid supports in response to an external perturbation. We introduce the temperature-dependent liquid elasticity length, which is the range of elastic interaction in a liquid. We propose that the first and second crossovers take place when this length becomes equal to the values of the medium-range length and system size, respectively.

We first note that in a perfect crystal, there are two fundamental lengths, lattice constant a and system size L . In a disordered system like liquid, there is an additional length d_m , which corresponds to the medium-range order, and is defined by local packing. d_m is on the order

of 10 Å, the characteristic size of decay of correlations in a disordered media.

We now introduce the liquid elasticity length d_{el} . Unlike a solid, a liquid does not support static stresses. However, it supports stresses at high frequencies in a solid-like manner [2]. These frequencies correspond to times smaller than system relaxation time τ . If d_{el} is the distance over which interactions in a liquid are elastic, $d_{el} = c\tau$, where c is the speed of propagation of elastic interactions, and is approximately equal to the speed of sound. c is on the order of $c = a/\tau_0$, where τ_0 is the oscillation period, or inverse of Debye frequency ($\tau_0 = 0.1$ ps) and a is the interatomic separation of about 1 Å. We therefore find

$$d_{el} = \frac{\tau}{\tau_0} a \quad (1)$$

We note that d_{el} crosses, on lowering the temperature, all three fundamental lengths in a system. Since $\tau = \tau_0 \exp(V_0/kT)$ at high temperature, where V_0 is the high-temperature activation barrier, $d_{el} = a \exp(V_0/kT)$. At high temperature, d_{el} is on the order of interatomic distance a . On lowering the temperature, it increases to d_m . Because d_m is about 10 Å, we find from Eq. (1) that $d_{el} = d_m$ gives τ of about 1 ps. This is the first dynamic crossover discussed above. On lowering the temperature even further, Eq. (1) shows that d_{el} increases to L . In liquid relaxation experiments, L is typically 1-10 mm. According to Eq. (1), $d_{el} = L$ gives $\tau = 10^{-7} - 10^{-6}$, the second dynamic crossover. This points to the intriguing possibility to describe the most important changes in system's dynamics using only its three fundamental lengths.

To discuss why the two dynamic crossovers correspond to $d_{el} = d_m$ and $d_{el} = L$, we first recall the previous discussion how a liquid relaxes stress in response to an external perturbation. Some time ago, Orowan introduced "condordant" local rearrangement events [10]. A concordant local rearrangement is accompanied by a strain agreeing in direction with the applied external stress, and reduces the energy and local stress (see Figure 1). A discordant rearrangement, on the other hand, increases the energy and local stress. This has led to a general re-

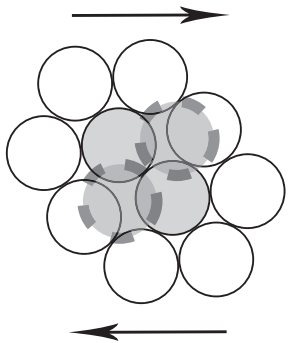


FIG. 1: Orowan's illustration of a concordant local rearrangement. Solid and dashed lines around the shaded atoms correspond to initial and final positions of a rearrangement, respectively. Arrows show the direction of external stress.

sult that stress relaxation by earlier concordant events leads to the increase of stress on later relaxing regions in a system [10]. Goldstein applied the same argument to a viscous liquid [11]: consider a system under external stress which is counterbalanced by stresses supported by local regions. When a local rearrangement to a potential minimum, biased by the external stress, occurs (a concordant event), this local region supports less stress after the event than before; therefore, other local regions in the system should support more stress after that event than before [11].

Lets consider stress relaxation in a liquid under external perturbation (e.g., pressure or temperature). To illustrate the argument of Orowan and Goldstein above, we consider a system under stress and discuss the dynamics of pressure-induced local relaxation events (LREs), i.e those events that come in addition to thermal rearrangements. In a simple model of parallel springs under external stress, a relaxation by a concordant event can be modeled as an appearance of a spring with a reduced spring constant. It is easy to show [12], that after the introduction of n weaker springs, which corresponds to n concordant relaxation events in a real system, the increase of stress on a current unrelaxed spring Δp is proportional to the current number of events n , $\Delta p \propto n$. We now invoke the previous discussion about the activation barrier V for a LRE in a real liquid. It has been argued that V is essentially the elastic energy [2, 13, 14, 15]. In the Shoving model, for example, V is given by the work of the elastic force needed to shove aside the surrounding liquid in order for a relaxation event to take place [15]. Therefore the increase of activation barrier is proportional to the increase of elastic force due to the increase of pressure, Δp , on a current local rearranging region, and we find $V \propto \Delta p \propto n$. This provides the feed-forward interaction mechanism between LREs, in that activation barriers increase for later events. This mechanism is general, and does not depend on the choice of the

spring model which we used here for illustration purposes only.

It is important to discuss the condition under which the feed-forward interaction mechanism becomes operative on lowering the temperature. Let t_s be the time needed for elastic interaction to propagate between LREs, d the distance between LREs, c the speed of sound, and τ_0 the oscillation period, or inverse of Debye frequency ($\tau_0 = 0.1$ ps). Because $c = a/\tau_0$, $t_s = \tau_0 d/a$. Relaxation time τ , which is also the time between two consecutive relaxation events [2], increases on lowering the temperature. It is easy to see that at high enough temperature, when $\tau = \tau_0$, $t_s > \tau$ is always true because $d/a > 1$. In this case, local events relax independently of each other, because at high temperature, the time between the events is shorter than the time needed for elastic interaction to propagate between them. Because events are independent, we obtain the expected high-temperature result that relaxation is Debye (exponential) in time [12] and Arrhenius in temperature. On cooling the system down, a certain temperature always gives the opposite condition: $t_s \leq \tau$. When the time between local relaxation events exceeds the time of propagation of elastic interaction between the events, the discussed above feed-forward interaction mechanism becomes operative. In other words, when $t_s \leq \tau$, local relaxation events do not relax independently, but “feel” the presence of each other. We have recently showed how this picture gives rise to SER [12]. Note that d_{el} sets the maximal distance between those LREs which are involved in the feed-forward interaction mechanism: $t_s = \tau$ gives $d = a\tau/\tau_0 = d_{el}$.

We are now ready to discuss how the first dynamic crossover appears in this picture. Lets denote τ_1 the time of this crossover. As follows from the above discussion, τ_1 is equal to the time needed for elastic interaction to propagate between neighbouring LRE. Let d be the distance between two adjacent LRE. Its value is on the order of 10 interatomic distances, or medium range order d_m . Because $\tau_1 = d_m/c$ and $c = a/\tau_0$, we find

$$\tau_1 = \frac{d_m}{a} \tau_0 \quad (2)$$

We observe that τ_1 is the relaxation time of the system which corresponds to $d_{el} = d_m$ (see Eq. (1)).

Because $\tau_0 = 0.1$ ps and d_m/a are roughly system- and temperature-independent, Eq. (2) predicts that τ_1 is a universal parameter, independent on temperature or system type. This is consistent with experimental findings [3, 4, 5, 6, 7]. If d/a is on the order of 10 and $\tau_0 = 0.1$ ps, we find from Eq. (2) that τ_1 is about 1 ps, in good agreement with the experimental value of τ_1 in 1–2 ps range [3, 4, 5, 6, 7].

To discuss the second dynamic crossover, we elaborate on how, on lowering the temperature, the increase of the radius of the feed-forward interaction increases ac-

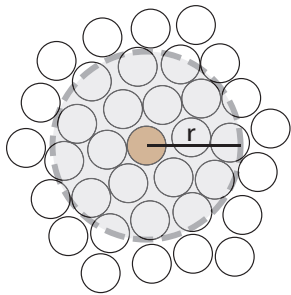


FIG. 2: Illustration of the feed-forward interaction mechanism between local relaxation events. This mechanism operates within the sphere of radius $r = d_{el}/2$, which increases according to Eqs. (1-2). Shaded and open circles represent local relaxing regions inside and outside, respectively, of the interaction sphere.

tivation barriers for LRE. As discussed above, the maximal distance between those LREs which are involved in the feed-forward interaction mechanism is equal to the elasticity length d_{el} . According to Eq. (1), d_{el} is on the order of interatomic distances at high temperature, but increases on lowering the temperature. The qualitative argument, which is sufficient for this discussion, proceeds as follows, and is illustrated in Figure 2. Let N be the number of LREs, induced by external perturbation (i.e. those in addition to thermally-induced events) in the sphere of diameter d_{el} . As discussed above, remote concordant LREs result in the increase of stress, Δp , on a current local region. Because this increase is additive, Δp increases with N . Since N increases with d_{el} , Δp is a monotonously increasing function of d_{el} . As discussed above, the activation barrier $V \propto \Delta p$. Hence we find that V is a monotonously increasing function of d_{el} .

The second dynamic crossover originates in this picture when, on lowering the temperature, d_{el} reaches the system size L . At high temperature, only small parts of the system are elastic, $d_{el} \ll L$, as in the case of the first crossover when $d_{el} = d_m$. When $d_{el} = L$ on lowering the temperature, all LREs in the system are involved in the feed-forward interaction. Hence $d_{el} = L$ marks the transition of the system from being partially to wholly elastic, and should manifest itself as a qualitative change in the liquid's dynamics.

Another interesting prediction from this picture comes from the observation that at $d > L$, reducing the temperature further has a weak effect on V , because at this point the increase of V is related to the feed-forward interaction between temperature-induced events only, but not due to the increase V by way of the increase of d_{el} . As a result, the system is expected to show a crossover to more strong behaviour. Note that in this picture, the second crossover depends on system size. If, for example, the increase of

V is described by the Vogel-Fulcher-Tamman law, the divergence at a finite temperature is avoided because as the system crosses over to more strong behaviour, the divergence is pushed to zero temperature. Only the infinite system does not have the second dynamic crossover, and has the divergence at a finite temperature.

Experimentally, there is ample evidence for the dynamic crossover in many systems. Most direct evidence comes from the sharp kink in the dielectric function [8]. The crossover to the lower slope of relaxation time, with the effect that glass transition becomes retarded, is observed [16], in agreement with the prediction from our picture. Other experiments include NMR relaxation data, which detect a similar dynamic crossover [17], the crossover in the relaxation of cage sizes in the positron annihilation experiments [18] and changes of non-ergodicity parameter [19].

If τ_2 is relaxation time at the second crossover, $d_{el} = L$ gives (see Eq. (1)):

$$\tau_2 = \frac{L}{a} \tau_0 \quad (3)$$

Eq. (3) predicts that, similar to τ_1 , τ_2 is a universal parameter, independent on temperature or system type. This is consistent with experimental findings [8, 9, 16, 17, 18, 19]. Typical values of L used in the experiments are 1–10 mm, which is dictated mostly by the experimental setup. For example, smaller system sizes can be associated with surface effects, while larger system sizes can involve temperature gradients. Using this range of L and $\tau_0 = 0.1$ ps, we find from Eq. (3) that $\tau_2 = 10^{-7} - 10^{-6}$ s, in good agreement with experimental values [8, 9]. Note that at the second $d_{el} = L$ crossover, $1/\tau_2$ has the meaning of the eigenfrequency of the system.

We note that relaxation time $\tau_2 = 10^{-7} - 10^{-6}$ s corresponds to viscosities η of $10^3 - 10^4$ Pa·s. These are much larger than room-temperature viscosities of familiar liquids like water, ethanol, olive oil or glycerol, for which $\eta = 10^{-3} - 10^1$ Pa·s. For these liquids, Eq. (1) gives d_{el} in the range of 1–1000 Angstroms. Viscosity of honey ($\eta = 10^2$ Pa·s) still falls behind the viscosities that correspond to relaxation time τ_2 . Honey's elasticity length is $d_{el} = 0.01$ mm. Very viscous tar ($\eta = 10^4$ Pa·s, $d_{el} = 1$ mm) has relaxation time close to τ_2 and elasticity length comparable to the experimental length scale. Only extremely viscous pitch ($\eta = 10^8$ Pa·s, $d_{el} = 10$ m) has relaxation time that exceeds τ_2 and elasticity length in excess of the experimental length scale. Hence these examples illustrate that although the second crossover is way above the glass transition (see below), it corresponds to quite high values of viscosity. They also give the feeling for the actual values of the introduced elasticity length in real liquids.

In this picture, no dynamic crossover takes place at T_g , consistent with the experimental observations. Ac-

cording to Eq. (1), $\tau(T_g) = 10^3$ s corresponds to d_{el} of 1000 kilometers, which explains why the two dynamic crossovers are seen way before T_g is reached. In other words, the absence of a dynamic crossover in the vicinity of T_g is due to the imbalance between our typical experimental times and sample sizes: at typical experimental time, the elasticity length is more than 8 orders of magnitude larger than the typical experimental length. In this context, we note that thermodynamic anomalies at T_g are sensitive to cooling rates and observation times. Were the thermodynamic parameters to be measured at higher cooling rates and shorter experimental times, they would show the changes at temperatures that correspond to relaxation time τ_2 .

In summary, we have introduced liquid elasticity length, and showed that when it becomes equal to the medium-range length and system size, two universal dynamic crossovers take place. The values of crossovers are fixed by a , d_m and L , three fundamental lengths in a disordered system. From the physical point of view, the first crossover can be said to be more fundamental since it does not depend on system size L . Our finding represents a new interesting link between geometry and dynamics of the system.

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